ABSORPTION MEASUREMENTS OF
CARBON MONOXIDE LASER RADIATION BY WATER VAPOR

July 1972

Prepared by

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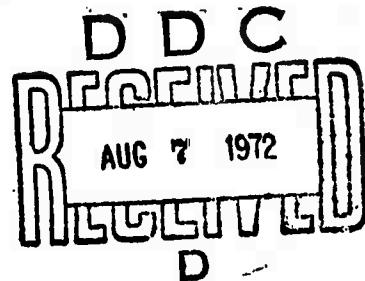
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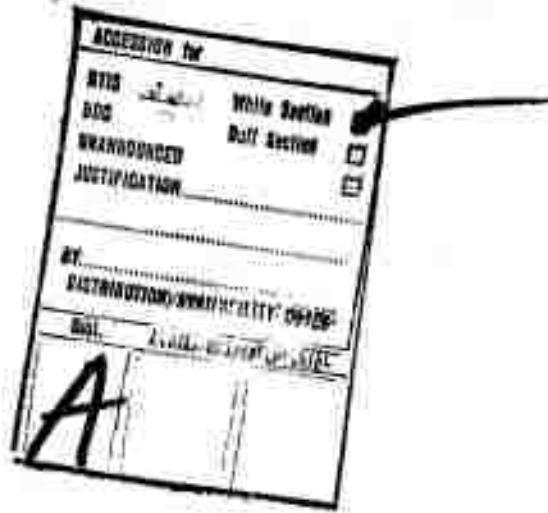
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13. ABSTRACT

An intracavity water vapor cell in conjunction with a CO laser was used to experimentally measure the absorptive losses introduced for 19 of the laser emission lines. The results indicate that the existing theoretical models are inadequate for predicting actual absorptance values for water vapor partial pressures in excess of 100 torr. The accepted spectral location of at least one water vapor absorption line was shown to be erroneous. A pressure broadening gas such as nitrogen was shown to increase the differential absorptive loss introduced by the water vapor for CO laser rotational lines. This result enhances the applicability of an intracavity water vapor cell as a device for limiting CO laser oscillation to lines having high atmospheric transmission.

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ABSTRACT

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I. INTRODUCTION

One of the reasons for the current interest in the CO laser is the coincidence of some of its emission frequencies with the 5 μm atmospheric transmission bands.[1-3] The primary atmospheric absorber in this spectral region is water vapor. A unique method has been experimentally demonstrated which permits laser action to occur only on the spectral lines having high atmospheric transmission.[4,5] The method uses an intracavity water vapor cell to prevent oscillations from building up on the unwanted low atmospheric transmission lines. Is is desirable to optimize this approach for low pressure CO lasers and to utilize it in high pressure-high gain CO lasers. This requires the determination of the actual intracavity loss introduced by the water vapor content, temperature, and additive broadening gases. The objective of the investigation, reported here, was to experimentally measure the monochromatic absorptive losses introduced by an intracavity water vapor cell as a function of various parameters, and to correlate the results with calculated values in order to determine the applicability of the existing theoretical models.

The results of experimental measurements of the absorptive losses introduced by an intracavity water vapor cell are shown to differ from the existing theory.[6-9] It is also shown that the differential absorptive losses introduced for the CO laser rotational lines can be increased by

the addition of a line broadening gas (such as nitrogen) to the vapor cell, thereby improving upon the line selection capability of the water vapor.

II. THEORY

The water vapor spectral region of interest for CO laser radiation absorption is the ν_2 band. The absorption of infrared radiation in this region by water vapor has been studied both theoretically and experimentally by many investigators.[6-41] The theoretical details of molecular absorption as pertaining to water vapor may be found in several texts;[42,43] only the basic relationships associated with the present investigation will be discussed in this section.

The molecular absorption coefficient for a single collision broadened spectral line is given by the Lorentz relation[1,6,10,41,42,44]

$$k(\nu) = S\alpha/\pi[(\nu - \nu_o)^2 + \alpha^2] \qquad (1)$$

where

S = total line intensity

α = half width of Lorentz line (cm^{-1})

ν_o = frequency of line center (cm^{-1})

ν = frequency of interest (cm^{-1}).

These parameters vary with temperature, pressure, and gas composition. The temperature variation of the line intensity is due to the temperature

dependence of the partition function and the Boltzmann factor and is given by[1, 6, 41]

$$S = S_o(T_o/T)^m \exp\left|-1.4388E''[(T_o - T)/T_oT]\right| \qquad (2)$$

where

$$T_o = \text{reference temperature } (^oK)$$

$$T = \text{temperature of absorbing gas } (^oK)$$

$$S_o = \text{line intensity at } T_o$$

$$E'' = \text{lower rotational energy level of the transition}$$

in the absorbing gas (cm^{-1})

$$m = \text{exponential factor resulting from the temperature}$$

dependence of the partition function which

depends on the absorbing gas.

For water vapor, which is an asymmetric top molecule, m = 1.5.[45]

The temperature dependence of the line width is given by[1, 6, 38, 40]

$$\alpha(T) = \alpha(T_o)[T_o/T]^n. \qquad (3)$$

The value of n varies with the gas composition and the actual transition involved in the absorption. For H_2O-H_2O collisions Benedict and Kaplan[7] give an average value of n = 0.896; for H_2O-N_2 collisions the average value is n = 0.62.[38]

The pressure and gas composition dependence of the half width of a water vapor spectral line for a water vapor/nitrogen mixture is given by[6,8,9]

$$\alpha = [BP(H_2O) + P(N_2)]\alpha_o \qquad (4)$$

where

B = self-broadening coefficient with respect to nitrogen broadening

$P(H_2O)$ = partial pressure of water vapor (torr)

$P(N_2)$ = partial pressure of nitrogen (torr)

α_o = water vapor half width at a nitrogen pressure $P_o (cm^{-1}/torr)$.

The value of B varies from line to line and Benedict and Kaplan[7] give an average value of B = 5.49.

Since the absorptance at any designated frequency results not only from absorption lines near that frequency but from the wings of lines at a distance from that frequency, the effect of all spectral lines within a reasonable distance must be considered and thus the transmittance through a gas having an absorption coefficient given by (1) is

$$T(\nu) = \exp\left\{-\left[\sum_i k_i(\nu)\right]\delta\right\} \qquad (5)$$

where i designates an individual spectral line. δ is the absorber thickness of the gas; this is just the vapor density multiplied by the path

length. The units of δ depend on those of S and α and are discussed in the Appendix. The absorptance is

$$A(\nu) = 1 - T(\nu). \qquad (6)$$

In order to provide convenient access to the pertinent water vapor parameters when calculating the water vapor absorption of CO laser spectral lines corresponding to the experimental conditions, a magnetic tape was obtained from the Institutes for Environmental Research, ESSA, Boulder, Colorado.[46] This is essentially the same data as given by Benedict and Calfee[28] except the magnetic tape data is for a temperature of $296^{\circ}K$ instead of $287.7^{\circ}K$ and the line widths are about 20% wider corresponding to more recent calculations. The updated line width in terms of the original line width is found from[47]

$$\alpha' = 1.2(\alpha - 0.032) + 0.032. \qquad (7)$$

This relationship is for a temperature of $296^{\circ}K$. However, according to a consensus of current investigators, the original half widths appear to be more accurate and thus (7) was inverted in the computer model for this investigation to permit utilization of the magnetic tape data.

It was decided to consider the contributions from all water vapor lines within 50 cm^{-1} of the CO laser frequency of interest when calculating the absorptance. A CDC 6600 computer was used to make

the computations. The relationships resulting from the above discussion
of which the basic computer model was comprised are listed:

$$A(\nu) = 1 - \exp\left\{-\left(\sum_i S_i(\nu_o)\alpha_i(\nu_o)/\pi[(\nu - \nu_o)^2 + \alpha_i^2(\nu_o)]\right)\delta\right\} \qquad (8)$$

$$S_i(\nu_o) = S_i'(\nu_o)[296/T]^{1.5}\exp\left\{-1.4388E_i''(\nu_o)[296 - T)/296T]\right\} \qquad (9)$$

$$\alpha_i(\nu_o) = (1.316 \times 10^3)\left\{5.49P(H_2O)[296/T]^{0.896} + P(N_2)[296/T]^{0.62}\right\} \times$$

$$\left\{[\alpha_i'(\nu_o) - 0.032]/1.2 + 0.032\right\} \qquad (10)$$

$$\delta = NL/V \qquad (11)$$

where

$S_i'(\nu_o)$ =   line strength at ν_o in $cm^{-1}/(molecules/cm^2)$
from ESSA tape

$E_i''(\nu_o)$ =   energy level of lower state of transition ν_o in
cm^{-1} from ESSA tape

$\alpha_i'(\nu_o)$ =   nitrogen broadened line width at ν_o in cm^{-1}/atm
from ESSA tape

N   =   number of water vapor molecules

V   =   volume in cm^3

L   =   path length in cm.

The typical half widths of the CO spectral lines for the low pressure laser used in the investigation are 0.001 cm^{-1},[48] which is approximately two orders smaller than the usual water vapor spectral half widths; therefore, in the calculations the CO laser emission was assumed to be monochromatic.

III. EXPERIMENT

The basic experimental configuration for measuring the absorptance of the CO laser spectral lines by water vapor is illustrated in Figure 1. The setup consists of two resonator configurations with a common low pressure CO gain medium. Q-switched, single wavelength operation is achieved with a rotating mirror and a diffraction grating giving two pulses for every complete rotation of the mirror. The first pulse occurs when resonator 1 (rotatatable Brewster plate) is aligned and the second pulse occurs when resonator 2 (absorption cell) is aligned. With the cell evacuated and the Brewster plate at Brewster's angle, the two pulses are identical; when water vapor at a particular temperature and pressure is admitted to the cell, pulse 2 will decrease in energy due to the absorptive loss introduced. The Brewster plate can then be rotated to introduce an equivalent reflective loss in resonator 1 such that pulse 1 has the same energy content as pulse 2. The amount of loss introduced by the cell is determined from the calibrated loss curve of a Brewster plate as a function of its angle.

DIFFRACTION GRATING

OUTPUT COUPLER

100% REFLECTOR

CO DISCHARGE
TUBE

ABSORPTION CELL

100% REFLECTOR

2

OFF-ANGLE ROTATABLE
BREWSTER PLATE

1

ROTATING MIRROR
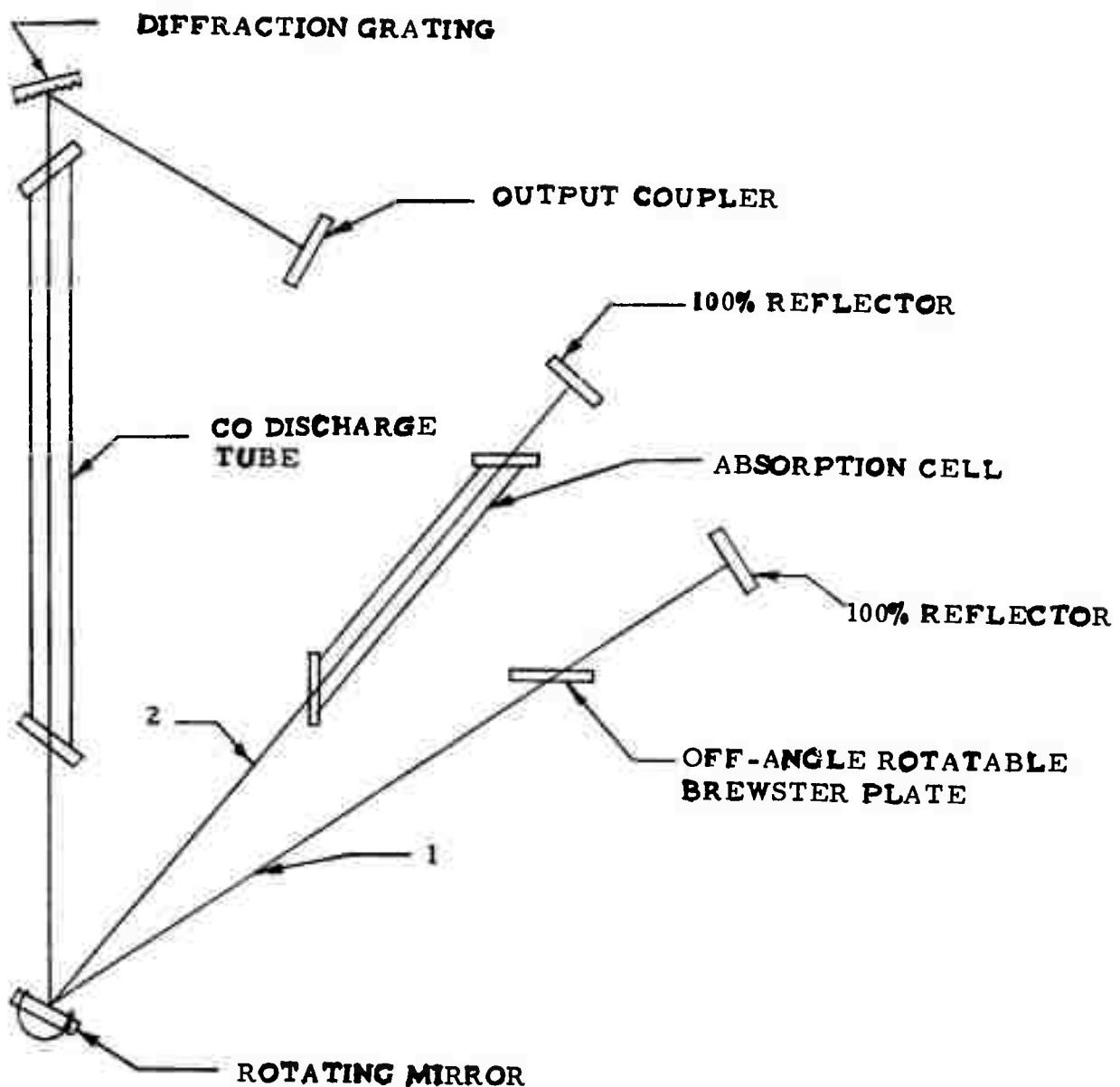
Figure 1.   Experimental Configuration for Absorption
Measurements.

Figure 2 shows the actual pulses obtained for the 10-9 P(8) CO laser line for a particular set of water vapor parameters. The time scale in these figures is 1 μsec/div. Figure 2a shows a multiple sweep exposure of the two pulses in the calibration mode; the absorption cell is evacuated and the Brewster plate is at Brewster's angle. Figure 2b shows both pulses when the cell contains 242 torr of water vapor at 150°C and the Brewster plate is at Brewster's angle; note the decrease in energy content of pulse 2. Figure 2c shows both pulses after the Brewster plate has been rotated to insert an equivalent amount of reflective loss (6.9%).

The absorption cell is constructed of stainless steel with a high temperature ceramic interior coating; its volume is 1310 cm^3. It has a 2.5 cm diameter clear aperture and an optical path length of 71 cm, and has two calcium fluoride windows. The cell temperature can be varied from 25°C to 200°C and a uniform temperature from one end to the other can be maintained to $\pm$ 1°C. The cell pressure can be varied from 0.01 torr to 5 atmospheres. The system can provide water vapor up to 2 atmospheres and has provisions for introducing additional absorbing or broadening gases up to a total pressure of 5 atmospheres.

The diffraction grating used for wavelength selection was a Bausch and Lomb, 150 grooves/mm, 6 μm blaze wavelength grating (Cat. No. 35-53-06-880). The setup was such that the first order of the diffracted beam from the

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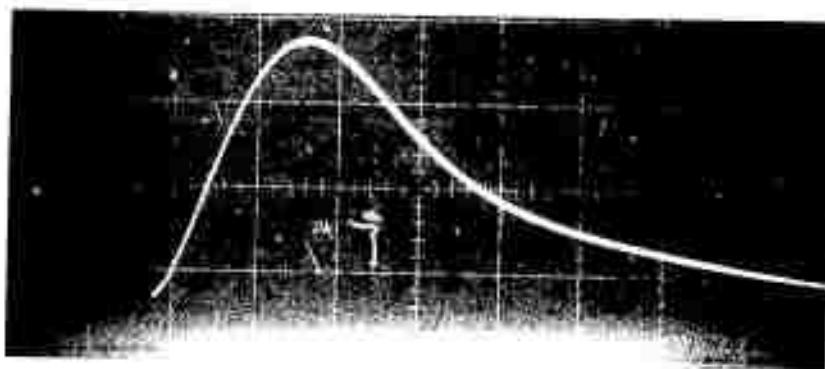
2a. Vapor Cell - Evacuated
     Brewster Plate - at Brewster's Angle.
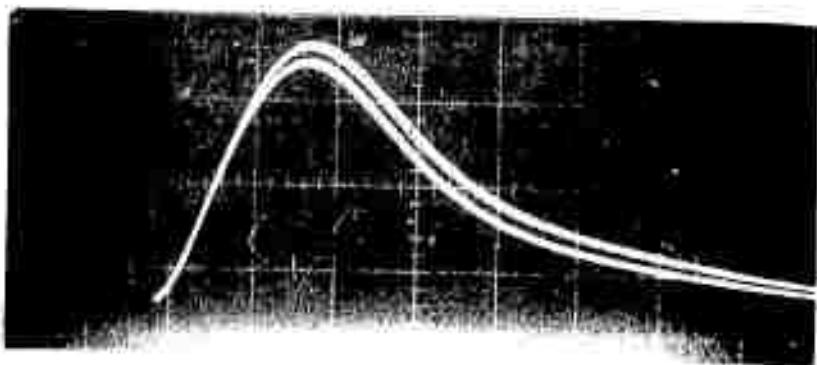
2b. Vapor Cell - 242 Torr of 150°C Water Vapor
     Brewster Plate - at Brewster's Angle.
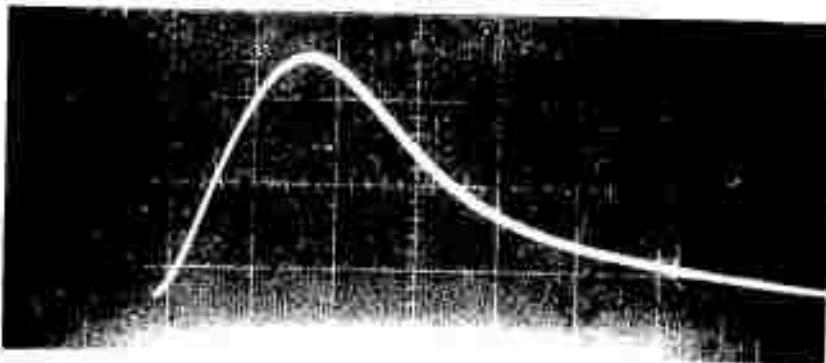
2c. Vapor Cell - 242 Torr of 150°C Water Vapor
     Brewster Plate - Rotated to provide 6.9%
                            Reflective Loss.

Figure 2. 10-9P(8) Q-Switched CO Laser Pulses from Resonator 1
           and Resonator 2 (1 μ sec/div.)

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grating was aligned with the flat surfaced output coupler; thus, as the grating was rotated to allow laser oscillation on any designated CO spectral line, the output beam was always directed along the same path, eliminating the need for frequent alignment of the beam steering optics into the spectrometer.

The spectrometer used in the setup was a 1.0 m, f/8 Czerny-Turner mounting (Jarrell-Ash Model No. 78-466). Liquid nitrogen-cooled In:Sb detectors (Cryogenics Associates) were used. The rotatable Brewster plate was a 0.375 inch thick, by 3.0 inch diameter calcium fluoride window (Harshaw Chemical) having a 1.38 mr wedge angle. The cell pressure was measured with a high temperature differential pressure transducer (Viatran Model No. 304) in conjunction with a signal conditioner (Action Instruments Model 4051).

The determination of the water vapor content of the cell for a particular set of parameters is described in the Appendix.

The low pressure CO gain medium utilized a 160 cm axial discharge, liquid nitrogen-cooled, double wall pyrex tube with sodium chloride Brewster windows. Typical operating conditions involved partial pressures as follows:

$$CO \ = \ 0.53 \text{ torr}$$

$$N_2 \ = \ 0.40 \text{ torr}$$

$$H_e \ = \ 5.76 \text{ torr}$$

$$O_2 \ = \ 0.01 \text{ torr}$$

The discharge current was 10 ma. There were adjustable irises at each end of the tube to provide for transverse mode control of the laser. Uniform temporal shape of the pulses for each frequency of operation was obtained by adjustment of the mode selecting irises in conjunction with variation of the rotating mirror speed (variable from 0 to 200 rps).

IV. DISCUSSION OF RESULTS

The results of the experimental measurements and theoretical calculations are presented in Tables I to VII. The symbol > signifies that the actual loss could not be measured because: (1) the absorptive loss was sufficient to eliminate pulse 2 thereby giving no reference for the adjustment of the rotatable Brewster plate for pulse 1, or (2) vignetting of the laser beam occurred due to the rotatable Brewster plate. The value designated by this symbol is the largest measurable loss before vignetting occurred or before pulse 1 was eliminated. Vignetting did not always occur at the same loss setting due to differences in the mode diameter for each spectral line. The symbol < signifies that the actual loss could not be measured because of the insensivity of loss measurements near the Brewster angle. The value designated by this symbol is the smallest distinguishable loss. All of the absorptance measurements were repeatable to within $\pm$ 0.01.

The measurements and calculations were performed for 19 of the CO spectral lines. The frequencies used in the calculations were from reference 48; however, when another investigator's frequencies were

used[49] no significant differences were observed.

Tables I, II, and III illustrate the broadening effect of nitrogen on the water vapor absorption lines. In all three cases the water vapor content is essentially the same (0.0048 pr. cm) and the gas temperature is constant (150°C). As the nitrogen partial pressure is increased from zero to two atmospheres, the measured and calculated absorptance values for all but one of the CO lines increase in approximately the same manner. A comparison of the values in these tables indicates that the theoretical model for these lines provides a reasonable description of the absorption mechanisms for this set of parameters. The one exception to this conclusion is the 7-6 P(13) CO line. Examination of the absorptance for this line shows that the measured absorptance increases with increasing amounts of nitrogen, while the calculated value first increases with one atmosphere of nitrogen and then decreases with two atmospheres. The decreasing of the calculated absorptance values for this line with increasing nitrogen is observed again in Tables IV and VI. An explanation of this effect is given in the discussion of these tables.

Tables IV and V demonstrate the self-broadening effect of water vapor on its absorption lines. When comparing the values of these tables with those of Table I, it is apparent that the increase in absorptance is due to more than just an increased number of water vapor molecules in the cell giving a greater absorber thickness. However, it is also obvious

TABLE I.   Absorptance Losses for CO Laser Radiation
Due to an Intracavity Water Vapor Cell

$P(H_2O)$ = 99 torr

$P(N_2)$ = 0

T   = $150^{\circ}C$

δ = 0.0048 pr. cm.

CO LASER SPECTRA		ABSORPTANCE	
Identification	Frequency (cm^{-1})	Measured	Calculated
10-9 Band			
P(14)	1854.921	< 0.010	0.007
P(10)	1870.607	> 0.364	0.305
P(9)	1874.445	< 0.010	0.007
P(8)	1878.249	< 0.010	0.008
9-8 Band			
P(14)	1880.336	< 0.010	0.009
P(13)	1884.342	0.045	0.089
P(12)	1888.315	0.032	0.045
P(11)	1892.255	0.035	0.021
P(10)	1896.162	0.029	0.027
P(9)	1900.035	< 0.008	0.004
P(8)	1903.875	0.024	0.073
8-7 Band			
P(14)	1905.829	0.011	0.008
P(12)	1913.878	0.009	0.013
P(10)	1921.794	0.092	0.099
P(9)	1925.703	0.038	0.009
7-6 Band			
P(14)	1931.396	< 0.008	0.004
P(13)	1935.473	< 0.008	0.120
P(12)	1939.516	0.008	0.009
P(10)	1947.503	< 0.005	0.008

TABLE II.   Absorptance Losses for CO Laser Radiation
Due to an Intracavity Water Vapor Cell

$P(H_2O) = 99$ torr

$P(N_2) = 763$ torr

$T = 150^{\circ}C$

$\delta = 0.0048$ pr. cm.

CO LASER SPECTRA		ABSORPTANCE	
Identification	Frequency (cm^{-1})	Measured	Calculated
10-9 Band			
P(14)	1854.921	0.012	0.018
P(10)	1870.607	>0.364	0.573
P(9)	1874.445	0.014	0.019
P(8)	1878.249	0.014	0.021
9-8 Band			
P(14)	1880.336	0.014	0.024
P(13)	1884.342	0.179	0.183
P(12)	1888.315	0.114	0.107
P(11)	1892.255	0.058	0.052
P(10)	1896.162	0.064	0.067
P(9)	1900.035	<0.008	0.010
P(8)	1903.875	0.035	0.053
8-7 Band			
P(14)	1905.829	<0.008	0.018
P(12)	1913.878	0.025	0.028
P(10)	1921.794	0.282	0.228
P(9)	1925.703	0.032	0.023
7-6 Band			
P(14)	1931.396	<0.008	0.009
P(13)	1935.473	<0.008	0.136
P(12)	1939.516	0.026	0.023
P(10)	1947.503	<0.008	0.019

TABLE III.   Absorptance Losses for CO Laser Radiation
Due to an Intracavity Water Vapor Cell

$P(H_2O)$ = 100 torr

$P(N_2)$ = 1515 torr

T   = 151°C

δ = 0.0048 pr. cm.

CO LASER SPECTRA		ABSORPTANCE	
Identification	Frequency (cm^{-1})	Measured	Calculated
10-9 Band			
P(14)	1854.921	0.027	0.028
P(10)	1870.607	>0.364	0.700
P(9)	1874.445	0.018	0.031
P(8)	1878.249	0.023	0.034
9-8 Band			
P(14)	1880.336	0.023	0.038
P(13)	1884.342	0.227	0.228
P(12)	1888.315	0.194	0.165
P(11)	1892.255	0.100	0.083
P(10)	1896.162	0.132	0.104
P(9)	1900.035	<0.008	0.017
P(8)	1903.875	0.056	0.059
8-7 Band			
P(14)	1905.829	0.040	0.028
P(12)	1913.878	0.033	0.042
P(10)	1921.794	>0.364	0.331
P(9)	1925.703	0.032	0.036
7-6 Band			
P(14)	1931.396	<0.005	0.015
P(13)	1935.473	0.008	0.117
P(12)	1939.516	0.025	0.037
P(10)	1947.503	0.014	0.030

TABLE IV.   Absorptance Losses for CO Laser Radiation
              Due to an Intracavity Water Vapor Cell

$P(H_2O)$ = 248 torr

$P(N_2)$ = 0 torr

T   = $150^{\circ}C$

δ = 0.0121 pr. cm.

CO LASER SPECTRA		ABSORPTANCE	
Identification	Frequency (cm^{-1})	Measured	Calculated
10-9 Band			
P(14)	1854.921	0.070	0.043
P(10)	1870.607	>0.364	0.879
P(9)	1874.445	0.066	0.047
P(8)	1878.249	0.072	0.052
9-8 Band			
P(14)	1880.336	0.072	0.058
P(13)	1884.342	>0.282	0.397
P(12)	1888.315	0.369	0.245
P(11)	1892.255	0.172	0.125
P(10)	1896.162	0.214	0.157
P(9)	1900.035	0.038	0.026
P(8)	1903.875	0.120	0.128
8-7 Band			
P(14)	1905.829	0.060	0.045
P(12)	1913.878	0.123	0.067
P(10)	1921.794	>0.364	0.473
P(9)	1925.703	0.076	0.055
7-6 Band			
P(14)	1931.396	0.038	0.023
P(13)	1935.473	0.064	0.307
P(12)	1939.516	0.085	0.056
P(10)	1947.503	0.055	0.047

TABLE V.   Absorptance Losses for CO Laser Radiation
Due to an Intracavity Water Vapor Cell

$P(H_2O) = 327$ torr

$P(N_2)$ = 0 torr

T   = 148°C

δ = 0.0161 pr. cm.

CO LASER SPECTRA		ABSORPTANCE	
Identification	Frequency (cm^{-1})	Measured	Calculated
10-9 Band			
P(14)	1854.921	0.187	0.073
P(10)	1870.607	>0.359	0.968
P(9)	1874.445	0.146	0.080
P(8)	1878.249	0.157	0.088
9-8 Band			
P(14)	1880.336	0.172	0.049
P(13)	1884.342	>0.222	0.547
P(12)	1888.315	>0.342	0.388
P(11)	1892.255	0.342	0.207
P(10)	1896.162	>0.308	0.258
P(9)	1900.035	0.106	0.045
P(8)	1903.875	0.244	0.171
8-7 Band			
P(14)	1905.829	0.129	0.075
P(12)	1913.878	0.257	0.111
P(10)	1921.794	>0.308	0.668
P(9)	1925.703	0.168	0.095
7-6 Band			
P(14)	1931.396	0.060	0.040
P(13)	1935.473	0.132	0.350
P(12)	1939.516	0.157	0.096
P(10)	1947.503	0.132	0.080

TABLE VI.   Absorptance Losses for CO Laser Radiation
Due to an Intracavity Water Vapor Cell

$P(H_2O)$ = 244 torr

$P(N_2)$ = 1520 torr

T   = 151°C

δ = 0.0118 pr. cm.

CO LASER SPECTRA		ABSORPTANCE	
Identification	Frequency (cm^{-1})	Measured	Calculated
10-9 Band			
P(14)	1854.921	0.161	0.087
P(10)	1870.607	>0.308	0.968
P(9)	1874.445	0.132	0.098
P(8)	1878.249	0.149	0.109
9-8 Band			
P(14)	1880.336	0.129	0.119
P(13)	1884.342	>0.308	0.491
P(12)	1888.315	>0.364	0.446
P(11)	1892.255	0.369	0.244
P(10)	1896.162	>0.364	0.302
P(9)	1900.035	0.056	0.055
P(8)	1903.875	0.195	0.155
8-7 Band			
P(14)	1905.829	0.126	0.088
P(12)	1913.878	0.183	0.130
P(10)	1921.794	>0.364	0.717
P(9)	1925.703	0.161	0.115
7-6 Band			
P(14)	1931.396	0.049	0.049
P(13)	1935.473	0.095	0.227
P(12)	1939.516	0.148	0.116
P(10)	1947.503	0.100	0.097

TABLE VII. Absorptance Losses for CO Laser Radiation due to an Intracavity Water Vapor Cell

$P(H_2O)$ = 202 torr

$P(N_2)$ = 1517 torr

T   = 149°C

δ = 0.0098 pr. cm.

CO LASER SPECTRA		ABSORPTANCE	
Identification	Frequency (cm^{-1})	Measured	Calculated
10-9 Band			
P(14)	1854.921	0.111	0.068
P(10)	1870.607	>0.364	0.935
P(9)	1874.445	0.100	0.076
P(8)	1878.249	0.114	0.084
9-8 Band			
P(14)	1880.336	0.097	0.092
P(13)	1884.342	>0.236	0.426
P(12)	1888.315	>0.364	0.365
P(11)	1892.255	0.252	0.194
P(10)	1896.162	0.364	0.242
P(9)	1900.035	0.031	0.042
P(8)	1903.875	0.153	0.126
8-7 Band			
P(14)	1905.829	0.095	0.069
P(12)	1913.878	0.142	0.102
P(10)	1921.794	>0.364	0.626
P(9)	1925.703	0.129	0.089
7-6 Band			
P(14)	1931.396	0.036	0.038
P(13)	1935.473	0.080	0.196
P(12)	1939.516	0.106	0.090
P(10)	1947.503	0.080	0.075

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that the theoretical model does not adequately describe the effect of self-broadening on the absorptance. Since the measured values in Tables IV and V are consistently higher than the calculated values, the average value of 5.49 for the self-broadening coefficient as discussed in Section II, is shown to be inadequate in predicting water vapor absorption for the spectral region covered in this investigation. Thus it appears that the higher the partial pressure of water vapor in the cell, the more inadequate is the theoretical model in describing the spectral absorptance. This conclusion is substantiated by Tables I, IV, and V. The only varying parameter for the data of these three tables is the water vapor content or partial pressure; the nitrogen partial pressure is zero and the temperature is constant (150°C). Examination of the ratios of measured to calculated absorptance values illustrates the insufficiency of the theoretical model for increasing water vapor content; the average ratio for Table I (99 torr) is 0.98; the average ratio for Table IV (248 torr) is 1.41; and the average ratio for Table V (327 torr) is 1.98. The average ratios for Tables III, VI and VII give the same indication; the nitrogen partial pressure in this case is essentially constant (1520 torr), as is the temperature (150°C). The average ratio for Table III (100 torr) is 0.91; the average ratio for Table VI (202 torr) is 1.25; and the average ratio for Table VII (244 torr) is 1.31. There-fore, in order to more accurately describe the spectral absorption of monochromatic radiation in the 5 μm region by high pressure water

vapor, a more accurate estimate of the effective self-broadening coefficient is required.

As mentioned earlier, the absorptance of the 7-6 P(13) laser line is inconsistent with respect to pressure variation. This is especially noticeable in Tables IV and VI. The water vapor pressure is essentially constant (245 torr) for both of these cases, as is the temperature (150°C). As the partial pressure of nitrogen is increased from zero to 1520 torr, the measured absorptance increases from 0.064 to 0.095, while the calculated value decreases from 0.307 to 0.277. In addition to this anomalous behavior, for both sets of conditions, only the 7-6 P(13) line has a measured absorptance value less than that which is calculated. The frequency of the 7-6 P(13) line is given as 1935.473 cm^{-1}. Reference 25 lists a highly absorbing water vapor line at 1935.440 cm^{-1} with a half-width of 0.036 cm^{-1}/atm. When broadening mechanisms are considered, the halfwidth of this line for Table IV parameters is 0.046 cm^{-1} and for Table VI parameters is 0.096 cm^{-1}. Therefore, in both cases the CO laser line falls well within the halfwidth of the 1935.440 cm^{-1} water vapor line. Considering absorption due to this single spectral line only, the strong line absorption approximation can be used. This may be obtained from Equation (1), i.e., when a frequency falls near the line center of a strongly absorbing line, the $(\nu - \nu_o)$ term can be neglected and the absorption coefficient becomes:

$$k(\nu) = S/\pi\alpha. \tag{12}$$

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Thus as α increases, k decreases. Conversely, when a frequency falls several halfwidths away from the line center, the α^2 term can be neglected and the absorption coefficient is approximated by:

$$k(\nu) = S\alpha/\pi(\nu - \nu_o)^2. \tag{13}$$

In this case as α increases, k increases.

Since the 7-6 P(13) CO laser line falls well within the halfwidth of the 1935.440 cm^{-1} water vapor line, the strong line approximation is valid. This would indicate that as the halfwidth of the absorbing line was broadened by increasing the nitrogen partial pressure, the absorptance would decrease; from Tables IV and VI this is what the calculations demonstrate. However, experimentally this is not the case, since as the nitrogen pressure increases, the absorptance increases. Therefore it is obvious that the spectral location of the 7-6 P(13) CO line, the 1935.440 cm^{-1} water vapor line, or both, are in error. Other investigators have indicated that individual water vapor line locations may be uncertain to as much as 2 cm^{-1} while the CO spectral frequencies have been identified to $\pm 0.006 \text{ cm}^{-1}$. [1] The resulting conclusion is that the location of the 1935.440 cm^{-1} water vapor line is mislabeled.

The most significant results of this investigation are that the relative absorptive losses for rotational lines in a particular vibrational band of the CO laser due to the intracavity water vapor cell can be manipulated by the addition of a broadening gas such as nitrogen. An example of this

effect is illustrated using Tables IV and VI where the only varying parameter is the partial pressure of nitrogen. The effect can be best demonstrated with two rotational lines having significantly different absorptances. These lines should be in the same band. The 9-8 band has two such lines; the P(11) and the P(9). The ratios of the measured absorptive losses for these lines are 4.53 $[P(N_2) = 0$ torr$]$ and 6.59 $[P(N_2) = 1520$ torr$]$; thus the differential absorption for these two lines was increased due to broadening of the water vapor absorption lines by the 2 atmospheres of nitrogen. This effect again demonstrates the inadequacy of the theoretical predictions because the ratios of the calculated values for the same lines are 4.81 $[P(N_2) = 0$ torr$]$ and 4.44 $[P(N_2) = 1520$ torr$]$. Therefore the theory indicates a decrease in the differential loss while the experimental results show an increase. It is also of interest to note the effect of nitrogen broadening on the differential absorption losses for two adjacent rotation lines, e.g. the 9-8 P(8) and 9-8 P(9) lines. The ratios of measured values for these lines are 3.16 $[P(N_2) = 0$ torr$]$ and 3.48 $[P(N_2) = 1520$ torr$]$, showing the increase even for two adjacent lines. The theoretical model again would predict the opposite with ratios of calculated values 4.92 $[P(N_2) = 0$ torr$]$ and 2.82 $[P(N_2) = 1520$ torr$]$.

V. SUMMARY

The results of this investigation indicated that the existing theoretical models give a reasonable prediction for monochromatic absorptive losses introduced by an intracavity water vapor cell for CO lasers when the water vapor content is low, i.e. partial pressures of less than 100 torr. However when the water vapor content is greater than this amount the results show that an insufficient description of the self-broadening mechanisms through the self-broadening coefficient precludes accurate prediction of absorptive losses. As the partial pressure of water vapor is increased, theoretical calculations become more and more inadequate in estimating the actual losses. The experimental measurements also indicated that the spectral location of at least one water vapor line, as given in the literature, is incorrect.

The experimental results also demonstrated that a certain amount of control can be obtained over the differential absorptive losses introduced by the water vapor cell for rotational lines in a particular vibrational band. This desired effect results from the addition of a line broadening gas such as nitrogen to the vapor cell. This fact is extremely important in allowing laser action on only the CO spectral lines having high atmospheric transmission. The theoretical predictions alone would indicate a detrimental effect by the addition of nitrogen.

Considering the water vapor content required of an intracavity cell for CO laser line selection, it appears that the experimental measurements are a requisite until a more adequate evaluation of the water vapor self-broadening coefficient is available to allow accurate theoretical prediction of the losses.

APPENDIX

The water vapor concentration in the absorption cell for a particular set of parameters was determined using the specific volume relationship as a function of temperature and pressure as given by Keenan and Keyes.[50]

$$v = 4.5504T/p + B \qquad (A-1)$$

where

$$p = \text{partial pressure of water vapor in atm}$$

$$v = \text{specific volume in } cm^3/g$$

$$T = \text{temperature in } {}^{o}K = \tau^{-1}$$

and

$$B = B_o + B_o^2 g_1(\tau)\, p + B_o^4 g_2(\tau)\tau^3 p^3$$

$$- B_o^{13} g_3(\tau)\tau^{12}p^{12}$$

$$B_o = 1.89 - 2641.62\tau 10^{80870\tau^2}$$

$$g_1(\tau) = 82.546\tau - (1.6246 \times 10^5)\tau^2$$

$$g_2(\tau) = 0.21828 - (1.2697 \times 10^5)\tau^2$$

$$g_3(\tau) = 3.635 \times 10^{-4} - (6.768 \times 10^{64})\tau^{24}.$$

Since this calculation is required for each set of parameters, a computer code was established for conveneince. The input data for the code consisted of the partial pressure of water vapor in torr and the temperature of the

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